SAMPLING AND ANALYSIS OF PREPARED CANE FOR ITS ASH CONTENT WITH REFERENCE TO ESTIMATING SOIL LEVELS IN CANE

By M. A. BROKENSHA
Sugar Industry Central Board
and P. MELLET
Sugar Milling Research Institute

Abstract

Sampling and analysis of prepared cane for its ash content is described and evaluated. The results show the sampling and analytical procedures to be without bias and the precision of a test for a consignment of cane has been found to be ± 0,32 units of ash % cane, the coefficient of variation being 8,8 per cent. Use of the ash % cane data in arriving at an estimate of the level of soil in the cane is discussed.

Introduction

The level of soil in cane delivered to some factories and the resultant wear to milling plant and disruption to operations has prompted investigation into the development of a method for assessing the soil content of cane consignments. To this end the Sugar Milling Research Institute and Huletts Sugar Limited[1] have been investigating an ashing method as a means of estimating soil levels in prepared cane. With this procedure the soil content of a cane sample is taken as the ash residue obtained from ashing the sample under specified conditions, minus an ash amount deemed to be the ash content of the cane alone. Work on this latter aspect, viz., the assessment of the ash content of the cane alone, has still to be completed.

As part of the overall project the Sugar Industry Central Board, at the request of the South African Sugar Technologists' Factory Control Advisory Committee, has planned and conducted tests to determine the accuracy and precision of cane sampling procedures in terms of ash content assessment.

The results of these investigations are reported below.

Analytical

(*a*) *General*

Essentially the procedure is to ash a sample of prepared cane to constant mass in a muffle furnace at 850°C.

(*b*) *Ashing container*

Initially stainless steel dishes (SS 316), with perforated lids, were used for ashing of samples. Dimensions were 150 mm long x 80 mm wide x 30 mm deep. It was, however, found that these dishes underwent thermal degradation at the elevated temperature used (850°C), and serious errors were introduced in weighings.

Fused silica basins of 400 cm^3 capacity (Gallenkamp Catalogue No. B 11) are now used for ashing. Dimensions are 145 mm diameter and 62 mm deep. Perforated lids used with these basins are made from SS 316 and although the lids undergo thermal degradation, this is of no consequence as the lids do not feature in any of the weighing stages. The lids are perforated with 2 mm holes having a pitch of 17,5 mm and fit the basins loosely.

The silica basins initially show a loss in mass, on average 0,06 g per analysis, but after approximately 10 ashings stability is attained.

(*c*) *Sample size*

Generally the larger the sample the greater the precision of analysis but with the ashing container in use at present larger samples also result in longer ashing times. For example, a 50 g sample requires a total ashing time of 45 minutes to achieve constant mass whereas a 100 g sample requires 120 minutes.

Tests were conducted comparing the precision of analysis for 50 g samples with that obtained for 100 g samples. The test procedure was to mix a sample of prepared cane, and from this to withdraw ten pairs of 50 g and 100 g sub-samples. The sub-samples were then ashed in accordance with the procedure described in 2 (*e*) below. The results are shown in Table 1.

TABLE 1
Comparison of ash values obtained by ashing 50 g and 100 g samples respectively

	50 g sample (Ash % dry sample)	100 g sample (Ash % dry sample)	Difference 50 g − 100 g
	7,21	7,11	+0,10
	6,49	7,11	−0,62
	6,59	6,79	−0,20
	7,72	7,22	+0,50
	7,62	6,95	+0,67
	6,79	7,43	−0,64
	6,59	7,11	−0,52
	6,38	7,11	−0,73
	6,69	6,79	−0,10
	6,59	6,95	−0,36
Mean	6,87	7,06	−0,19
SD	±0,48	±0,20	±0,49
CV	7,0	2,8	SE ±0,15
n	10	10	10

SD = Standard deviation
CV = Coefficient of variation
n = Number of analyses
SE = Standard error

From the results shown in Table 1 it is seen that there is no significant difference in accuracy between the two sample sizes. However, the precision of the 100 g sample is superior to that of the 50 g sample.

(*d*) *Ashing time*

As mentioned above an ashing time of 2 hours is required to obtain constant mass when using a 100 g sample in the fused silica basin. Earlier work with the stainless steel dishes which were 30 mm deep as opposed to 62 mm deep for the silica basins showed that constant mass could be attained at 45 minutes for the 100 g sample. Clearly the greater depth of the silica basin is resulting in a less efficient air flow over the cane sample and a more suitably shaped container should see ashing times well below 1 hour for the 100 g sample.

(*e*) *Procedure*

Note: Each basin must be "cured" prior to ash determinations by repeating 10 cycles of heating for 2 hours then cooling.

This is done to eliminate the initial mass loss as mentioned in (*b*) above.

(i) Weigh 100 g of sample, ± 0,01 g, into a clean, dry and pre-weighed basin.

(ii) Cover the basin with the lid and put in a well vented muffle furnace, set at 850° C, for 30 minutes.

(iii) Remove the lid from the basin and leaving the door of the furnace slightly open (about 10 mm), to facilitate air circulation, heat for a further 90 minutes.

(iv) Replace the lid on the basin, remove basin from the furnace and cool for 2 minutes on an asbestos sheet before transferring to a desiccator for 90 minutes.

(v) Place the basin, with lid, on the balance, then remove the lid and weigh the basin plus ash.

(vi) If the ash % is expressed on sample, the result can now be calculated directly, but if ash % is expressed on a dry sample basis a moisture determination must be performed on a subsample taken from the original at the same time when the sample for ashing is taken.

(*f*) *Accuracy*

Lionnet and Wagener[1] have tested the response of the method to varying amounts of sand of known ash content. The procedure was to mix a prepared cane sample and then sub divide into five sub-samples. One sub-sample was ashed as is, while known masses of sand (98% ash content) were added to each of the others and the sub-samples then ashed. The results are given in Table 2.

It is seen that the method responds directly to the variations in ash present in the sub-samples.

(*g*) *Precision*

Analytical precision was determined by analysing 60 samples in duplicate. Each cane sample consisted of about 3 kg of cane which had been taken from the cane sampling point at the mill and subsequently prepared in two batches (each of 1,5 kg) in the sample shredder[2]. In the laboratory the two batches were thoroughly mixed on the bench and two 100 g samples (A and B) withdrawn for ashing.

Results of the 60 comparisons are given in Table 3.

From the standard deviation of differences the standard deviation of a test is obtained as follows:

(i) In terms of ash % cane
Standard deviation of a test
$= \pm 0{,}18 \div \sqrt{2}$
$= \pm 0{,}13$ ash % cane

(ii) In terms of ash % dry matter
Standard deviation of a test
$= \pm 0{,}61 \div \sqrt{2}$
$= \pm 0{,}43$ ash % dry matter

(*h*) *Comparison of the "basin" and "crucible" methods*

The procedure described in (*e*) above, but using 50 g of sample instead of 100 g of sample with commensurate reduction in ashing time from 120 minutes to 45 minutes was compared with an alternate procedure used in the past by the Sugar Milling Research Institute.

The proposed method will be referred to as the "basin" method whilst the alternative Sugar Milling Research Institute procedure used in the past will be referred to as the "crucible" method.

The procedure for the crucible method is as follows:

(i) Drying a sample of prepared cane in a moisture oven at 105°C for 6 hours and at the same time determining its moisture content.

(ii) Milling the dried sample by means of a small laboratory mill (e.g. Wiley Mill) through a screen with pore openings of 0,85 mm.

(iii) Ashing 3–4 g of the milled sample in a small fused silica crucible (Gallenkamp Catalogue No. CWC—290—110Y) at 800 C° for 3 hours.

(iv) Determining the moisture content of the milled sample in parallel with the ash determination.

(v) Calculation of ash % dry sample.

The above procedure is tedious and not suitable for routine ash analysis. It was felt, however, that it would be useful to compare the two methods.

Twenty replicates were carried out on each of the four samples of shredded cane from four different mills. Procedure was to mix the main sample, divide into two halves and then proceed using the basin method on the one half and the crucible method on the other. Results are given in Table 4.

TABLE 2
Mass ash analysed versus mass ash calculated

Mass cane (1,47 ash %) (g) .	50,34	54,42	57,14	56,46	61,22
Sand added (98% ash) (g). .	0	2,5	5,0	7,5	12,5
Mass ash (g)					
Analysed	0,74	3,27	5,76	8,14	13,12
Calculated	—	3,25	5,74	8,18	13,15

TABLE 3
Analytical precision

	Ash % Cane			Ash % Dry Matter		
	A	B	A–B	A	B	A–B
Mean . .	2,42	2,45	−0,03	7,18	7,33	−0,15
SD . . .			±0,18			±0,61
n . . .			60			60

TABLE 4
Comparisons of ash values found by the basin method to those of the crucible method
Ash % dry sample

	UF		ME		IL	
	Basin	Crucible	Basin	Crucible	Basin	Crucible
Mean	6,89	6,81	3,70	3,99	5,52	5,99
SD	±0,469	±0,330	±0,203	±0,102	±0,192	±0,350
CV	6,8	4,8	5,5	2,6	3,5	5,8
n	20	20	20	20	20	20
	SZ		Combined		Overall Difference	
	Basin	Crucible	Basin	Crucible	Basin − Crucible	
Mean	5,54	5,87	5,41	5,66	Mean	−0,25
SD	±0,270	±0,338	±0,305	±0,298	SD	±0,47
CV	4,9	5,8	5,6	5,3	SE	±0,05
n	20	20	20	20	n	80

SD = Standard deviation
CV = Coefficient of variation
n = Number of analyses
SE = Standard error

It is seen from the results that overall there is very little difference in the precision obtained for each method but in terms of accuracy there is a significant difference between the two methods in that the crucible method gives a higher ash result than the basin method. However, it is felt that the crucible figure may have been elevated on account of fine fibrous dust, relatively low in ash, possibly being lost during the laboratory milling process.

Sampling Accuracy

Tests have been conducted to check that the sample taken by the cane sampler[2] (full width hatch) is representative of the cane consignment at that point on the elevator, i.e. just before entering the feed chute of the first milling unit. This evaluation has been achieved by repeatedly comparing the analysis of one hatch cut taken under normal operating conditions (dynamic sample) with that obtained from the complete slat load of cane withdrawn through the sampler with the hatch fully opened and the cane elevator stationary (static sample) — this latter sample being used as reference. Actual procedure for the static sample was to stop the elevator immediately after the

dynamic sample (in practice two to three slats would intervene) and then carefully position the complete slat load of cane above the hatch. The door would then be opened and all the cane on the slat would fall through.

In each case (dynamic and static) the full hatch sample was collected at the sample point. The cane was hand mixed on the sample table and duplicate samples taken. The duplicates were shredded and then combined and mixed together in the laboratory. Finally, duplicate samples were withdrawn for ash, as well as pol, brix and moisture analyses. (Duplicate analysis of a well mixed, shredded sample will give an indication of the analytical precision.)

The results of the dynamic versus static tests are summarised in Table 5 below. Each of the dynamic and static results reported is an average of the duplicate analytical comparisons. Table 3 above under analytical precision is a summary of the duplicate analytical comparisons. Only cane consignments with visible evidence of high soil content were selected for these tests.

It is seen from Table 5 that the hatch is without significant bias.

Sampling Precision

(*a*) *Procedure*

Only consignments in which the soil was visibly seen to be at a high level were selected for these tests. From each consignment two consecutive hatch cuts were taken with the hatch operating as normal. The complete fall-out from each hatch cut was then collected separately, hand mixed and duplicate sub-samples withdrawn. Duplicate sub-samples were then shredded and analysed individually. Repeated comparison of two hatch cuts (each cut result being the average of duplicate analyses) affords a means of determining the precision of the hatch.

Comparisons of two analyses from each cut allows a measure of the hand sub-sampling and analytical precision.

(*b*) *Precision of the hatch*

The results are given in Table 6 below:

TABLE 6
Cane sampler (full width hatch) precision

	Ash % cane			Ash % dry matter		
	A	B	A–B	A	B	A–B
Mean	3,62	3,68	−0,06	11,48	11,65	−0,17
SD			±1,02			±2,96
n			20			20

(i) In terms of ash % cane
standard deviation of a single hatch cut
$= \pm 1{,}02 \div \sqrt{2}$
$= \pm 0{,}72$ ash % cane

Under routine testing conditions at a mill with a crushing rate equal to the industrial average (200 tons per hour) there will be approximately nine hatch openings for an average (20 ton) consignment.

Therefore, precision of the hatch for a 20 ton consignment
$= \pm 0{,}72 \div \sqrt{9}$
$= \pm 0{,}24$ ash % cane

(ii) In terms of ash % dry matter
Precision of the hatch for a 20 ton consignment
$= \pm 0{,}70$ ash % dry matter

(*c*) *Hand sub-sampling and analytical precision*

The results are shown in Table 7.

TABLE 7
Hand-sub-sampling and analytical precision

	Ash % cane			Ash % dry matter		
	A	B	A–B	A	B	A–B
Mean	3,62	3,67	−0,05	11,43	11,71	−0,28
SD			±0,29			±1,13
n			40			40

(i) In terms of ash % cane the standard deviation of differences
$= \pm 0{,}29$

Therefore, standard deviation of a single analysis
$= \pm 0{,}29 \div \sqrt{2}$
$= \pm 0{,}21$ ash % cane

(ii) A similar calculation for the ash % dry matter will give:
Standard deviation of a single analysis
$= \pm 0{,}80$ ash % dry matter

TABLE 5
Cane sampler (full width hatch) bias check. (Felixton No. 1 tandem)

	Ash % cane			Ash % dry matter			Pol % cane		
	D	S	D–S	D	S	D–S	D	S	D–S
Mean	2,45	2,42	+0,03	7,31	7,23	+0,08	12,26	12,23	+0,03
SD			±0,40			±1,25			±0,18
SE			±0,07			±0,23			±0,03
t			0,43			0,35			1, 0
n			30			30			30
	Brix % cane			Fibre % cane			Moist % cane		
	D	S	D–S	D	S	D–S	D	S	D–S
Mean	14,65	14,63	+0,02	18,85	18,81	+0,04	66,51	66,56	−0,05
SD			±0,21			±0,34			±0,51
SE			±0,04			±0,06			±0,09
t			0,50			0,67			0,56
n			30			30			30

D = dynamic
S = static
SD = standard deviation
SE = standard error
t = significance figure according to Student's t test
n = number of tests

(*d*) *Calculation of the precision of a test*

Combining the results reported under 5 (*b*) and 5 (*c*) will give the precision of a test (standard deviation of a test) under the conditions given above.

(i) In terms of ash % cane
Standard deviation of a test
$= \sqrt{0{,}24^2 + 0{,}21^2}$
$= \pm 0{,}32$ ash % cane
Coefficient of variation
$= (0{,}32 \div 3{,}65)\ 100$
$= 8{,}8$ per cent

(ii) In terms of ash % dry matter
Standard deviation of a test
$= \sqrt{0{,}70^2 + 0{,}80^2}$
$= \pm 1{,}06$ ash % dry matter
Coefficient of variation
$= 9{,}2$ per cent

The above results do not include the imprecision contribution of the automatic cane sub-sampler[2] as it has not been possible to include this component in the procedure employed in the investigation.

However, the reduction in the overall precision through the addition of this component is likely to be small and will not materially alter the overall precision reported above.

Ash % "soil free" cane

As mentioned in the introduction, in order to arrive at an estimate of the soil content of the cane sample, it is necessary to deduct a value for the ash content of the cane itself. Unfortunately this is not a constant but will vary depending on factors such as type of soil on which the cane was grown, fertilizer usage, moisture content of the cane, proportion of tops and trash, etc.

Spencer and Meade[3] report ash per cent brix in mixed juice varies from 1,5 to 4,5 per cent. A limited number of tests by the SMRI[4] have found ash per cent brix in mixed juice to be of the order of 2 per cent. Data reported by Don[5] show ash per cent fibre for cane stalks to range from 0,7 to 1,6 per cent, ash per cent fibre in trash from 3,0 to 4,1 per cent, and ash per cent fibre in tops from 2,4 to 2,7 per cent. Thus, not only is there the problem of the range of the ash values that can be found in each component but also the relative proportions that components bear one to another in the cane sample. The level of moisture in the sample is not a problem as this can be taken into account in the calculations.

Using the above data as basis it can be shown that for the normal range of cane quality encountered the ash per cent "soil free" cane can range from 0,4 to 1,2 per cent. The data used in the determination of these limits are shown in Table 8.

TABLE 8
Ash % "soil free" cane

	Example 1		Example 2	
Component	Component % cane	Ash % component	Component % cane	Ash % component
Tops . . .	1,8	—	3,8	—
Fibre in Tops.	0,2	2,4	0,4	2,7
Trash . . .	3,6	—	10,0	—
Fibre in Trash	2,9	3,0	8,0	4,1
Stalk fibre. .	10,3	0,7	9,1	1,6
Total fibre .	13,4	—	17,5	—
Brix . . .	14,5	1,5	16,3	4,5
Moisture . .	72,1	—	66,2	—
Cane . . .	100	0,38	100	1,22

If a deduction of 0,80 ash per cent cane were used for a standard 69 moisture per cent cane the deduction necessary for the first example in Table 8 would have been 0,80 x (100 − 72,1) ÷ (100 − 69,0) = 0,72 instead of the actual figure of 0,38 ash per cent cane. Similarly the figure shown for the second example in Table 8 would have been reported as 0,87 instead of 1,22 ash per cent cane.

It can be shown that for very high levels of tops or trash the use of a standard deduction with appropriate adjustment for moisture level will not differ from the actual figure by more than 0,4 units of ash per cent cane — the calculated deduction underestimating the true deduction.

Although the above considerations are based on limited data, they do indicate the order of accuracy with which soil levels in cane can be estimated under the proposed procedure. It is necessary that investigations be conducted into ways of determining as accurately as possible the amount of ash to be deducted for the "soil free" cane.

Conclusion

The investigation has shown that the sampling and analysis of individual consignments for ash content is without bias and individual consignment analysis can be obtained with a precision (standard deviation of a test) of ± 0,32 units of ash per cent cane. Expressed as a coefficient of variation this is equal to 8,8 per cent.

Use of a 50 g sample instead of 100 g will result in a loss of precision. On the basis of the change in precision reflected in Table 1, the standard deviation of a test using a 50 g sample increases from ± 0,32 to ± 0,43 units of ash per cent cane. However this is compensated for by the appreciable reduction in ashing time required (using the silica basin) and hence muffle furnace capacity.

The analytical procedure is straightforward and can be handled by laboratory staff after a minimum of training.

The estimate of relative levels of soil by deducting an average figure (adjusted for the moisture content of the cane sample) for the ash content of the cane itself does give rise to errors, but as indicated will probably not exceed 0,4 units in extreme situations and will usually be less. This aspect requires further investigation in order to more accurately quantify the amount of ash present in the cane itself, apart from that present in the soil.

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